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## EUROPEAN PATENT APPLICATION

⑬ Application number: 87113242.9

⑮ Int. Cl. 4: C22C 19/05

⑭ Date of filing: 10.09.87

⑯ Priority: 12.09.86 US 907055

⑰ Date of publication of application:  
23.03.88 Bulletin 88/12

⑲ Designated Contracting States:  
AT BE CH DE ES FR GB IT LI SE

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㉓ High temperature nickel base alloy with improved stability.

㉔ A nickel-chromium-molybdenum base alloy characterised by exceptional structural stability when exposed at temperatures upwards of 1800°F (980°C) for prolonged periods of time, such as 10 000 hours.

EP 0 260 600 A2

## HIGH TEMPERATURE NICKEL BASE ALLOY WITH IMPROVED STABILITY

FIELD OF INVENTION

5 The subject invention is directed to a nickel-chromium-molybdenum (Ni-Cr-Mo) alloy, and particularly to a Ni-Cr-Mo alloy which manifests a combination of exceptional impact strength and ductility upon exposure to elevated temperature, e.g., 1000°C (1832°F), for prolonged periods of time, 3,000 hours and more, while concomitantly affording high tensile and stress-rupture strengths plus good resistance to cyclic oxidation at high temperature.

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INVENTION BACKGROUND

15 Essentially, the present invention is an improvement over an established alloy disclosed in U.S. Patent 3,859,060. This patent encompasses a commercial alloy known as alloy 617, a product which has been produced and marketed for a number of years. Nominally, the 617 alloy contains about 22% chromium, 9% molybdenum, 1.2% aluminum, 0.3% titanium, 2% iron, 12.5% cobalt, 0.07% carbon, as well as other constituents, including 0.5% silicon, one or more of boron, manganese, magnesium, etc., the balance being nickel. The virtues of alloy 617 include (i) good scaling resistance in oxidizing environments, including cyclic oxidation, at elevated temperature, (ii) excellent stress rupture strength, (iii) good tensile strength and ductility at both ambient and elevated temperatures, etc.

20 Alloy 617 also possesses structural stability under, retrospectively speaking, what might be characterized as, comparatively speaking, moderate service conditions. But as it has turned out it is this characteristic which has given rise to a problem encountered commercially for certain intended and desired applications, e.g., high temperature gas feeder reactors (HTGR). This is to say, when the alloy was exposed to more stringent operating parameters of temperature (1800°F) and time (1000-3000+ hours) an undesirable degradation in structural stability occurred, though stress rupture, tensile and oxidation characteristics remained satisfactory.

25 Apparently, what happened was that prior to the 1800°F/1000+ hour operating conditions, the test temperature for stability study was usually not higher than 1600°F. And if higher temperatures were considered, short term exposure periods, circa 100 hours, were used. Longer term periods (circa 10,000 hours or more) were used but at the lower temperatures, i.e., not more than 1300°F-1400°F.

30 Apart from temperature/time operating conditions, the problem would not surface because in many applications structural stability was not critically important, e.g., boats used for catalyst-grid supports, heat treating baskets, reduction boats used in refining certain metals, etc.

35 Accordingly, the problem became one of ascertaining the cause(s) for the stability deterioration at upwards of 1800°F-2,000°F for periods well exceeding 1000 hours, and evolving, if possible, a new alloy which would result in enhanced stability under such operating conditions but without incurring a detrimental sacrifice in stress-rupture/oxidation/tensile properties.

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THE INVENTION

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We have found that silicon and molybdenum when present to the excess can adversely affect the stability of Alloy 617. We have also found that carbon, if beyond the range specified below herein, can, 45 depending upon chemistry, exercise a negative influence. Moreover, it has been determined that grain size plays a significant, if not the major, role, grain size being influenced by composition and processing, particularly annealing treatment. Grain size, chemistry, particularly silicon, molybdenum and carbon, and annealing temperature are interrelated or interdependent as will become more clear infra. The invention herein involves the critical controlling of these related aspects.

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50 Generally speaking and in accordance with the present invention, the alloy contemplated herein contains about 7.5 to about 8.75 or 9% molybdenum, not more than 0.25% silicon, 0.05 to 0.15% carbon, about 19 or 20 to 30% chromium, about 7.5 to 20% cobalt, up to about 0.6% titanium, about 0.8 to 1.5% aluminum, up to about 0.006% boron, up to 0.1% zirconium, up to about 0.075% magnesium, and the balance essentially nickel. The term "balance" or "balance essentially" as used herein does not exclude the presence of other constituents, such as deoxidizing and cleansing elements, in amounts which do not

0.6% Ti

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adversely affect the basic properties otherwise characteristic of the alloy. In this connection, any iron should not exceed 5%, and preferably does not exceed about 2%, to avoid subverting stress-rupture strength at temperatures such as 2000°F. Sulfur and phosphorus should be maintained at low levels, say, not more than 0.015% and 0.03% respectively. In respect of other elements, the presence of tungsten can be tolerated up to about 5%, and copper and manganese, if present, should not exceed 1%, respectively.

In carrying the invention into practice, and in endeavoring to achieve consistent results, care must be exercised in respect of compositional control; in particular, molybdenum, silicon and carbon should be interrelated and controlled as indicated hereinafter. Silicon has been found to act subversively, particularly at high molybdenum and carbon contents. In retrospect, virgin materials were used in the research stage of Alloy 617. Thus, silicon was at a low level. But in commercial production scrap materials are used wherever possible to reduce costs. As a consequence, higher percentages of silicon would have been employed since the overall adverse effect of silicon in conjunction with molybdenum/carbon, grain size/annealing temperature at 1800-2000°F was neither known nor understood prior to the present invention. As indicated above, a typical commercial nominal silicon content is 0.5% and there are current commercial "specifications" where the silicon can be as high as 1% with molybdenum being as high as 11%.

Morphologically speaking, the subject alloy is of the solid-solution type and further strengthened/hardened by the presence of carbides, gamma prime hardening being minor to insignificant. The carbides are of both the  $M_2C_6$  and  $M_6C$  types. The latter is more detrimental to room temperature ductility when occurring as continuous boundary particles. The higher levels of silicon tend to favor  $M_6C$  formation. This, among other reasons, dictates that silicon be as low as practical though some amount will usually be present, say, 0.01%, with the best of commercial processing techniques.

Molybdenum, while up to 9% may be tolerated, should not exceed about 8.75% in an effort to effect optimum stability, as measured by Charpy-V-Notch impact strength and tensile ductility (standard parameters). This is particularly apropos at the higher silicon levels. As will be shown infra, molybdenum contents even at the 10% level detract from CVN impact strength, particularly at silicon levels circa 0.2-0.25%. Molybdenum contributes to elevated temperature strength and thus at least about 8% should preferably be present. Tests indicate that stress-rupture life is not impaired at the 2000°F level though a reduction (acceptable) may be experienced at 1600°F in comparison with Alloy 617. Given the foregoing, it is advantageous that the silicon and molybdenum be correlated as follows:

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	<u>% Silicon</u>	<u>% Molybdenum</u>
	0.01-0.1	less than 9
35	0.1-0.15	less than 8.75
	0.15-0.25	less than 8.5

With regard to carbon, a range of 0.05 to 0.1%, particularly 0.05 to 0.07%, is advantageous. Carbon contributes to stress-rupture strength but detracts from structural stability at high percentages. Low levels say, 0.03-0.04%, particularly at low molybdenum contents, result in an unnecessary loss of stress-rupture properties. Carbon also influences grain size by limiting the migration of grain boundaries. As carbon content increases, higher solution temperatures are required to achieve a given recrystallized grain diameter.

Where optimum corrosion resistance is required, chromium can be used up to 30%. But at such levels chromium together with molybdenum in particular may lead to forming an undesired volume of the embrittling sigma phase. It need not exceed 28% and in striving for structural stability a range of 19 to 23% is beneficial.

In addition to the foregoing, it has been determined that grain size has a marked influence on toughness. Chemistry and processing control, mainly annealing temperature, are interdependent in respect of grain size. While it has been customary to final anneal Alloy 617 at 2175 to 2200°F commercially, in accordance with the present invention annealing should be conducted below about 2150°F and above 2000°F. The effect of annealing temperature on a commercial size, 22,000 lbs., melt is given in Tables IV and V. An annealing temperature of, say 2200°F, promotes the formation of the coarser grains but stress-rupture properties are higher. On the other hand, very low annealing temperatures, say 1900-1975°F, offer a finer grain size but stress-rupture is unnecessarily adversely impacted. Accordingly, it is preferred that the

annealing temperature be from 2025 to less than 2150°F with a range of 2025 to about 2125°F being preferred. While the grain size may be as coarse as ASTM 0 or 00 where the highest stress-rupture properties are necessary, it is preferred that the average size of the grains be finer than about ASTM 1 and coarser than about ASTM 5.5; e.g., ASTM 1.5 to ASTM 4.

5 To give those skilled in the art a better appreciation of the invention, the following information and data are given:

14 kg vacuum induction laboratory heats were made, then forged at about 2200°F to 13/16 inch squares for hot rolling (2200°F) to 9/16 inch rounds. Representative compositions are given in TABLE I. Alloys AA through DD are outside the invention.

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TABLE I

Alloy	No.	C	Mn	Fe	Si	Ni	Cr	Al	Ti	Co	Mo	B	Zr
15	1	0.07:0.011:1.33:0.06:56.23:21.98:1.08:0.61:10.99:	7.60:0.004:0.014										
	2	0.11:0.005:0.74:0.04:54.90:22.54:1.17:0.48:11.89:	8.19:0.003:0.014										
	3	0.08:0.008:0.69:0.21:54.34:22.63:1.17:0.41:12.00:	8.47:0.002:0.014										
	4	0.13:0.008:0.67:0.22:54.43:22.73:1.22:0.41:12.01:	8.28:0.001:0.014										
20	AA	0.07:0.007:0.68:0.23:52.81:22.59:1.21:0.42:12.00:10.11:0.003:0.014											
	BB	0.11:0.008:0.67:0.23:52.51:22.71:1.21:0.41:12.00:10.33:0.002:0.014											
	CC	0.06:0.008:0.71:0.04:53.04:22.46:1.17:0.44:11.99:10.17:0.003:0.014											
	DD	0.12:0.009:0.69:0.04:52.58:22.76:1.19:0.43:11.97:10.29:0.002:0.014											

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Annealing temperatures were 2125°F and 2250°F, respectfully, the specimens being held thereat for 1 hour, then air cooled. The alloys were exposed at 1832°F (100°C) for 100, 1000, 3000 and 10,000 hours and air cooled as set forth in TABLE II which sets forth the data obtained i.e., grain size, Rockwell hardness (Rb), yield (YS) and tensile strengths (TS), elongation (El.), Reduction of (RA) and Charpy V-Notch Impact Strength (CVN), the latter serving to assess structural stability.

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TABLE II

Alloy No.	Chemistry		Anneal °F/hr	Exposure °F/hr.	ASTM GS #	Hard Rb	0.2%		RA %	Impact Strength CVN Ft-lb
							TS ksi	E1 %		
1	.07 .06	7.60	2125/1,A	1832/ 100,A	4-1/2 <sup>m</sup>	—	52.8	124.5	50.	57.5 >240.
			2125/1,A	1832/ 1,000,A	5	91.	47.9	125.0	48.	56.0 119.
			2125/1,A	1832/ 3,000,A	— <sup>m</sup>	92.5	47.3	123.0	48.5	54. 53.5
			2125/1,A	1832/10,000,A	4	90.5	48.2	120.3	50.	53.5 57.5
	.11 .04	8.19	2250/1,A	1832/ 100,A	0	86.	42.8	114.0	48.	42.5 103.
			2250/1,A	1832/ 100,A	1/2	88.	42.6	116.5	48.	44.5 109.
			2250/1,A	1832/ 1,000,A	—	90.	42.7	103.5	22.	21.* 69.
			2250/1,A	1832/ 3,000,A	00	86.5	43.	93.1	21.5	20. 57.
2	.11 .04	8.19	2250/1,A	1832/10,000,A	00	—	—	—	—	— 33.5
			2125/1,A	1832/ 100,A	9**	—	62.2	135.5	43.	50.5 92.
			2125/1,A	1832/ 1,000,A	6	92.	48.8	128.0	44.	52.0 109.
			2125/1,A	1832/ 3,000,A	— <sup>m</sup>	96.5	57.7	131.0	43.	50. 77.5
	.21 .47	8.47	2125/1,A	1832/10,000,A	4	92.5	46.6	123.	48.5	57.5 68.5
			2250/1,A	1832/ 100,A	2	87.	93.6	LR	48.	48. 91.
			2250/1,A	1832/ 1,000,A	—	44.3	111.0	59.	47.0	156.
			2250/1,A	1832/ 3,000,A	2	91.	46.3	123.0	44.	42.0 84.
3	.08 .21	8.47	2250/1,A	1832/10,000,A	0	93.	44.0	121.5	38.5	31.5 52.5
			2250/1,A	1832/10,000,A	4 <sup>m</sup>	89.	44.1	111.5	27.	25.5 40.5
			2125/1,A	1832/ 100,A	— <sup>m</sup>	86.	44.8	95.2	19.	16. 34.5
			2125/1,A	1832/ 100,A	5 <sup>m</sup>	—	51.6	124.5	51.	57. 123.0
	.21 .47	8.47	2125/1,A	1832/ 1,000,A	5	90.0	47.9	122.5	50.	56.0 117.0
			2125/1,A	1832/ 3,000,A	— <sup>m</sup>	93.	49.1	127.0	48.5	58. 66.0
			2125/1,A	1832/10,000,A	4 <sup>m</sup>	93.	49.1	123.5	50.	54. 61.
			2250/1,A	1832/ 100,A	0	86.5	44.9	114.5	50.	46.5 90.

\*\* grain size believed in error for unknown reasons

TABLE II (CONT'D)

Alloy No.:	Chemistry			Anneal °F/hr	Exposure °F/hr.	ASTM GS #	Hard Rb	0.2% YS ksi	TS ksi	EI %	RA %	Impact Strength CVN Ft-lb
	C	Si	Mo									
4	.13	.22	8.28	2125/1,A	1832/ 100,A	5-1/2	--	51.6	127.5	46.	49.0	79.0
				2125/1,A	1832/ 1,000,A	6	92.5	49.4	127.5	43.	53.5	87.0
				2125/1,A	1832/ 3,000,A	--	93.5	50.5	131.0	44.	53.5	69.5
				2125/1,A	1832/ 6 <sup>m</sup>	6-1/2	94.	51.9	130.	44.	54.	64.
				2125/1,A	1832/10,000,A	6	90	48.8	124.5	45.5	52	74
				2250/1,A		3-1/2	--	47.3	116.0	55.	47.0	119.0
				2250/1,A	1832/ 100,A	3-1/2	91.0	46.1	122.5	46.	48.0	72.0
				2250/1,A	1832/ 1,000,A	--	92.	45.6	122.0	35.5	31.	50.0
				2250/1,A	1832/ 3,000,A	2	90.5	46.4	108.	22.	21.	41.
				2250/1,A	1832/10,000,A	1	88	44.5	104.	23.	21.	38.5
AA	.07	.23	10.11	2125/1,A		5-1/2	--	51.8	123.0	53.	55.5	121.0
				2125/1,A	1832/ 100,A	5-1/2	91.0	48.0	121.5	44.	38.5	65.0
				2125/1,A	1832/ 1,000,A	--	93.0	46.4	123.5	48.5	51.5	62.5
				2125/1,A	1832/ 3,000,A	5	91.5	47.1	120.	48.5	54.	56.
				2125/1,A	1832/10,000,A	5	88.	46.2	115.5	50.5	55.	76.
				2250/1,A		1	--	43.5	103.5	67.	51.5	132.0
				2250/1,A	1832/ 100,A	0	87.5	43.8	98.5	24.	20.5	28.5
				2250/1,A	1832/ 1,000,A	--	88.5	43.6	72.6	8.5	8.	16.5
				2250/1,A	1832/ 3,000,A	1	86.5	41.6	80.9	14.	14.5	9.
				2250/1,A	1832/10,000,A	0	84.5	40.2	63.0	6.5	5.5	8.
BB	.11	.23	10.33	2125/1,A		7-1/2	--	55.9	129.5	46.	43.0	63.0
				2125/1,A	1832/ 100,A	5-1/2	93.5	53.0	127.5	43.	48.5	64.0
				2125/1,A	1832/ 1,000,A	--	95.5	49.8	126.0	44.	48.	67.5
				2125/1,A	1832/ 3,000,A	5	95.5	50.9	128.	43.	47.	53.
				2125/1,A	1832/10,000,A	6 <sup>m</sup>	91.5	48.8	121.5	45.	45.	50.5
				2250/1,A		3-1/2	--	48.6	114.5	55.	45.5	94.0
				2250/1,A	1832/ 100,A	3	92.0	48.1	115.5	27.	21.5	26.0
				2250/1,A	1832/ 1,000,A	--	93.	48.0	111.5	18.5	15*	22.5
				2250/1,A	1832/ 3,000,A	1/2	91.5	46.6	89.7	10.5	11	22.
				2250/1,A	1832/10,000,A	1	90.0	44.6	107.5	23.	19.5	19.

55 50 45 40 35 30 25 20 15 10 5

TABLE II (CONT'D)

Alloy No.	Chemistry C Si Mo	Anneal °F/hr	Exposure °F/hr.	ASTM		Hard Rb	0.2% YS ksi	TS ksi	E1 %	RA %	Impact Strength CVN Ft-lb
				GS	#						
CC	.06 .04	10.17	2125/1,A	4-1/2	---	50.7	120.0	56.	61.0	240.	
	2125/1,A	1832/ 100,A	4	87.5	43.8	114.0	46.	38.5	38.5	82.5	
	2125/1,A	1832/ 1,000,A	--	91.5	47.1	119.5	50.	47.5	47.5	80.	
	2125/1,A	1832/ 3,000,A	4	90.5	47.	118.	51.5	49.	49.	41.	
	2125/1,A	1832/10,000,A	4 <sup>m</sup>	86.	44.1	113.	51.5	48.	48.	74.5	
	2250/1,A	1832/	1	80.0	43.5	103.5	69.	60.0	60.0	240.	
DD	2250/1,A	1832/ 100,A	0	85.0	41.8	106.0	41.	32.0	32.0	--	
	2250/1,A	1832/ 100,A	--	85.5	41.5	105.0	41.	31.5	31.5	53.0	
	2250/1,A	1832/ 1,000,A	--	87.5	43.0	111.5	41.5	34.	34.	42.5	
	2250/1,A	1832/ 3,000,A	0	86.5	42.8	103.5	30.	27.	27.	42.	
	2250/1,A	1832/10,000,A	1/2	84.	42.6	97.0	28.	24.	24.	35.	
	2250/1,A	2125/1,A	5	54.0	132.0	46.	40.5	40.5	40.5	79.0	
DD	2125/1,A	1832/ 100,A	5-1/2	93.0	51.3	129.5	44.	49.5	49.5	80.0	
	2125/1,A	1832/ 1,000,A	--	94.0	50.9	127.0	45.5	53.0	53.0	65.5	
	2125/1,A	1832/ 3,000,A	4	95.	52.8	128.5	43.	40.	40.	67.	
	2125/1,A	1832/10,000,A	5	91.	48.4	120.5	47	47.5	47.5	66.	
	2250/1,A	2125/1,A	3-1/2	49.1	118.0	55.	45.5	45.5	45.5	110.0	
	2250/1,A	1832/ 100,A	3	92.0	48.4	124.0	41.	32.5	32.5	46.5	
DD	2250/1,A	1832/ 1,000,A	--	93.	48.6	105.5	16.5	15.*	15.*	36.0	
	2250/1,A	1832/ 3,000,A	1	92.	47.7	101.5	17.	14.	14.	30.	
	2250/1,A	1832/10,000,A	1-1/2	88.5	45.5	89.5	14.	13.	13.	29.	

A = Air Cooled

m = Mixed Grain

LR = Lost Reading

\* = Broke Outside Punch Marks

Concerning the data above given, Alloys AA and BB resulted in markedly lower impact levels than Alloys 1-4, especially low silicon, low molybdenum Alloys 1 and 2, particularly when annealed at 2250°F. Alloys AA and BB had, comparatively speaking, high percentages of both silicon and molybdenum together with a coarse grain varying from ASTM 0 to 1. Alloys CC and DD while better than AA and BB due, it is deemed to much lower silicon percentages, were still much inferior to Alloys 1-4 given a 2125°F anneal. While the Charpy-V-Notch impact data for Alloys AA-DD appear to be good for the 2125°F anneal, our investigations have indicated that with commercial size heats impact strengths for alloys of high molybdenum significantly drop off. Also, there is danger/risk of not controlling annealing temperature and the 2250°F anneal reflects what can be expected in terms of anticipated structural stability.

5 In Table III are reported stress rupture data for the Alloys In Table I. In this case the annealing temperature was 2150°F. While the stress (5KSI) used at 1832°F is fairly high for that temperature level, stress rupture properties for the alloys within the invention are satisfactory.

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TABLE III

5	Alloy No.	C	Si	Mo	ASTM GS #	Temp °F	Stress ksi	Life hrs.	EL %	RA %
10	1	.07	.06	7.60	7.5	1200	60	1317.5	24.5	26.5
						1400	30	651.5	53.	71.
						1600	14	407	68.5	89.5
						1832	5	29.4	51.	62.
15	2	.11	.04	8.19	5.	1200	60	453.7	10.5	14.
						1400	30	473.4	47.	45.
						1600	14	22.1	61.5	77.
						1832	5	24.	45.5	52.
20	3	.08	.21	8.47	5.	1200	60	203.6	16.	14.5
						1400	30	374.6	17.	44.
						1600	14	17.8	63.5	83.
						1832	5	114.1	38.	39.
25	4	.13	.22	8.28	6.5	1200	60	430.7	13.5	15.
						1400	30	424.1	35.5	65.5
						1600	14	26.0	91.5	69.
						1832	5	56.2	35.5	40.
30	AA	.07	.23	10.11	6.	1200	60	1468.3	22.5	24.
						1400	30	808.3	44.	76.5 <sup>(1)</sup>
						1600	14	30.9	92.	90.
						1832	5	62.2	57.	66.
35	BB	.11	.23	10.33	8.	1200	60	1729.	33.5	35.5
						1400	30	520.7	49.	72.
						1600	14	30.7	120.5	87.5
						1832	5	39.9	46.6	66.5
40	CC	.06	.04	10.17	7.	1200	60	655.8	18.5	20.5
						1400	30	643.3	40.	64.
						1600	14	42.2	79.	87.5
						1832	5	169.6	39.	33.5
45	DD	.12	.04	10.29	6.5	1200	60	2592.5	23.	28.
						1400	30	567.8	44.5	59.
						1600	14	124.3	65.5	82.
						1832	5	65.3	31.5	42.

(1) Pulled out of grips @ 32.9 hours. restarted.

50 Tables IV and V pertain to a 22,000 lb. commercial size heat which was produced using vacuum induction melting followed by electroslag refining. The material was processed into 3/4" dia. hot rolled rounds for testing and evaluation. The as-hot-finished rod stock was used for an annealing evaluation/grain size study evaluation. The composition of the heat Alloy 5, is given below in Table IV with annealing temperature and grain size reported in Table V.

TABLE IV

	<u>Element,</u>	<u>Wt.%</u>		<u>Element,</u>	<u>Wt.%</u>
5	chromium	-- 21.88		iron	-- 0.21
10	cobalt	-- 12.48		manganese	-- 0.01
	molybdenum	-- 8.62		boron	-- 0.002
15	carbon	-- 0.05		magnesium	-- 0.001
	silicon	-- 0.07		sulphur	-- 0.001
	aluminum	-- 1.26		phosphorus	-- 0.002
	titanium	-- 0.23		copper	-- 0.01
				nickel	-- 55.18

TABLE V

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	<u>Anneal 1 hour at Temperature</u>	<u>Followed By Water Quench</u>	<u>Grain Size,</u>	<u>ASTM Grain No.</u>
25	2000		7.5	
	2050		4.0	
	2100		1.5	
30	2125		1.5	
	2150		1.0	
	2175		1.0	
	2200		0	
35	2225		0	
	2250		0	

As reflected by Table V, given the chemistry in IV, an annealing temperature above 2175°, e.g. 2200°F, and above resulted in an excessively coarse grain structure whereas annealing at 2000°F gave too fine a grain. As indicated above herein, a final annealing should be conducted above 2000°F to about 2150°F.

The effect of annealing temperatures (2000°F, 2050°F, 2125°F, 2250°F) and grain size on structural stability as indicated by the Charpy-V-Notch test size is shown in Table VI, and is more graphically depicted in Figure 1. Table VI includes tensile properties, stress rupture results being given in Table VII.

Anneal Temp., (°F)	Exposure Temp., °F	Exposure Time, Hrs.	G.S. ASTM No.	HD, (Rb)	0.2% YS, (ksi)	TS, (ksi)	EI, (%)	RA, (%)	CVN, (Ft lb/s)
									25 20 15 10
<b>As Hot Rolled</b>									
2000	—	8	94	67	128	49	55.5		
	1550	7.5	94.5	56.2	123.5	50	63.	165	
	100	94	63.4	127.5	47	59	128		
	1,000	7.5	93.5	62.7	126.5	47	60.5	118	
	3,000	94.5	60.6	126.5	46	56.5	124		
	10,000	93.5	61.3	126.5	47	60*	114*		
1832	100	94	60.6	127	48.5	61.5	119		
	1,000	7.5	93	59.4	125.5	48	62	115	
	3,000	86	52.6	121	47.5	60	121		
	10,000	82.5	40.3	110.1	56	65			
2050	—	4	95.5	53.3	121.5	50.5	65.5	221	
	1550	100	92	54.1	120	48	56	119	
	1,000	92	54.2	121.7	49	61	130		
	3,000	90.5	54.3	121.9	51	63			
	10,000	90.5	52.7	120	51	61			
1832	100	92	51.8	120.5	51	63	136		
	1,000	92	52.5	120.6	51	62	122		
	3,000	51	120.3	52	62	114**, 106			
	10,000								
2125	—	1.5	83	39.8	101.5	71	75		
	1550	100							
	1,000								
	10,000								
1832	100	82	40.1	104.5	46	37	55		
	1,000	82	37.5	96.1	42	36.5	58		
	3,000	83	37.7	101.5	43.5	34.5	60		
	10,000	82	38.3	100.4	45	36	58		

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TABLE VI cont'd.

Anneal Temp. (°F)	Exposure Temp. °F	Exposure Time Hrs.	G.S. No.	0.2%		RA (%)	CVN (Ft lbs)
				ASTM (Rb)	HD (ks1)	YS (ks1)	TS (ks1)
2250	1550	-	0	81.5	37.8	95.9	76
			100	88	44.7	109	47
			1,000	87	44	113	48
			3,000	88	42.7	111.5	46.5
			10,000	84.5	41.2	109.6	49
1832	1000	100	82	38.3	98.2	42	32.5
			1,000	82	36.4	97.1	45
			3,000	81	36.1	85.7	32.5
			10,000	79	35.6	84.0	30
						26	32

HD = s hardness

Rb = Rockwell hardness, B scale

GS = grain size

\* = went to 1710°F/5 min. at 3200h  
\*\* = went to 1990°F for 1 hr. at 1700h

TABLE VII

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## Stress Rupture Properties

10	ASTM	Test	Test				
	Ann. Temp	G.S.	Temp.	Stress	Life	E1	RA
	<u>°F/1 h, WQ</u>	<u>No.</u>	<u>(°F)</u>	<u>(ksi)</u>	<u>(h)</u>	<u>(%)</u>	<u>(%)</u>
15	2000	7.5	1600	13	23.9	96.8	89.1
	2050	4.0			39.9	83	91.5
	2125	1.5			50.3	87	77.5
20	2250	0			47.2	85.5	69
	0	7.5	2000	3.0	14.2	137.5	80
25	2050	4.0			18.1	115.5	76
	2125	1.5			76.6	98	56.5
	2250	0			96.0	46	56.5

30 The impact energy data at 1832°F in Table VI confirms the superior results of a commercial size heat of an alloy composition/annealing temperature within the invention. For an exposure period of 10,000 hours and an annealing temperature of 2250°F, Alloy 5 manifested a borderline impact strength of 32 ft. lbs., versus, for example, 58 ft. lbs., when annealed at 2125°F. It is deemed that the impact energy level at 1832°F and 10,000 hours exposure should be at least 40 ft. lbs. and preferably 50 ft. lbs. although, as suggested above 30 ft. lbs. is marginally acceptable. The 2000°F anneal afforded high impact strength at 10,000 hours but as shown in Table VII stress-rupture life suffered, being 23.9 hours vs. 50 hours when annealed at 2125°F. The difference is even more striking at the 2000°F test condition.

35 Apart from the foregoing and based on welding data at hand, the instant alloy is deemed readily weldable using conventional welding practices as will be demonstrated below. As a matter of general observation from the tests conducted, no base metal microfissuring was observed in the heat affected zone (HAZ) of a Gas Metal Arc (GMA) weldment. This test resulted in a slight loss of strength in the as-welded and annealed condition as would be expected but, more importantly, the deposit exhibited greatly improved ductility and impact strength after exposure to aging temperature, giving corresponding properties for commercial Alloy 617. Gas shielded metal arc (GSMA) deposits made using filler metals of the invention 40 alloy as a core wire in a coated welded electrode manifested improved ductility and impact strength in comparison with weld deposits using filler metal of commercial Alloy 617. In this connection, a significant loss of ductility was experienced after exposure and this was attributed to the elements, notably carbon and silicon, introduced in the deposit by the flux coating. It is deemed that such constituents are sufficient to 45 induce high temperature reaction which are believed responsible for the ductility loss in the deposit.

50 With regard to the welding tests, plate 0.345 inch thick taken from hot band of Alloy 5 was annealed at both 1800°F and 2200°F to provide material of different grain sizes. (The 1800°F would not cause a change in grain size, the original grain size being ASTM 2.5). The 2200°F anneal (which is not a recommended annealing treatment) gave a grain size beyond about ASTM 00. This was done with the purpose that an alloy of limited weldability, given the variation in grain size, would be expected to manifest 55 some variation in base metal microfissuring. A weldment was deposited between two specimens of the plate (one of each anneal) by GMAW - spray transfer with 0.045 inch diameter filler metal from Alloy 5, the following parameters being used.

Diameter - 0.045" Joint Design - V-Butt - 60° Opening

Current - 220 amps      Voltage - 32 volts  
 Wirefeed - 423 ipm      Position - Flat - 1G  
 Flow Rate - 50 cfh      Travel Speed - 12 - 15 ipm (Manual)

5 Transverse face, root and side bend specimens, centered in both the weld and heat affected zones (HAZ) were tested, (i.e., usually 3 specimens were taken from the weld plate per test conditions. Liquid penetration inspection revealed no fissuring in the welds or the HAZ. Using specimens bent over a thickness twice that of the specimens (2T), only one face bend test showed any fissuring; however, the fissures did not intersect the fusion line and were thus deemed not weld related but were probably due to plate surface. No other fissuring was detected in either liquid penetration or metallographic examination.

10 Filler metals of Alloy 5 were made in wire diameters of 0.045 and 0.093 inch and then used in Gas Metal Arc Welding (GMAW) spray transfer and Gas Tungsten Arc Welding (GTAW), respectively. A third wire, 0.125 inch in diameter was used as a core wire for producing a covered electrode for Shielded Metal Arc Welding (SMAW). Room temperature impact data from weldments of each of the GMAW, GTAW and SMAW are reported in Table VIII with mechanical properties being given in Table IX. The parameters for 15 the GTAW and SMAW were as follows:

GTAW

Diameter - 3/32"  
 Electrode Type/Diameter - 2% Thoriated Tungsten / 3/32"

20 Current - 180 amperes DCEN  
 Voltage - 12-14 volts

Shielding Gas - Argon

Flow Rate - 25 cfh

Joint Design - V-Butt 60° Opening

Position - Flat - 1G

25 Travel Speed - 4-6 ipm (Manual)

SMAW

Diameter - 1/8"

Current - 90 amperes

Voltage - 23 volts

30 Joint Design - V-Butt - 60° Opening

Position - Flat - 1G

Travel Speed - 10-12 ipm (Manual)

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TABLE VIII

## Room Temperature Impact Data

Process	Condition A* Impact			Condition B* Impact			Condition C* Impact			Condition D* Impact		
	CVN (ft. lb.)	Lat. Exp. (mils)	Duct. Fract. (%)									
GMAW	214	81	100	222	no fracture	135	80	100	88	63	100	
		n.t.		n.t.	n.t.	139	80	100	82	58	100	
		n.t.		n.t.	n.t.	132	80		88	62	100	
GTAW	179.5	97	100	239	no fracture	113	78	100	68	60	100	
	158	104	100		n.t.	118	76	100	62	58	100	
	167	98	100		n.t.	114	81	100	63	59	100	
SMAW	54	50	100	91.5	79	100	31	26	100	21	21	
SMAW	46	45	100	113.0	76	100	30	29	100	18	19	
SMAW	52	46	100	85.5	71	100	28	28	100	21	19	

\*A = As Welded

\*B = Welded + Annealed 2200°F/1 h, WQ

\*C = Welded + Annealed 2200°F/1 h, WQ + Exposed 1550°F/1000 h, AC

\*D = Welded + Annealed 2200°F/1 h, WQ + Exposed 1832°F/1000 h, AC

Lat. Exp. = Lateral Expansion

Duct. Fract. = Ductile Fracture

n.t. = not tested

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 TABLE IX  
Room Temperature Tensile Data

10	Condition*	Process	0.2%			Red. of Area (%)	Hardness RB
			UTS (ksi)	YS (ksi)	Elong. (%)		
15	A	GMAW	102.2	65.5	50	63.1	94/95
	A	GMAW	104.1	63.4	50	57.0	90/91
	A	GMAW	105.4	64.9	47	55.6	92
	B	GMAW	104.0	46.4	65	70.9	82/83
20	C	GMAW	119.9	51.1	41	42.5	89/92
	D	GMAW	109.1	43.5	49	40.2	83/86
25	A	GTAW	109.2	71.4	44	60.0	94/96
	B	GTAW	106.8	45.6	61	71.1	84
	C	GTAW	120.4	50.6	46	51.9	89/91
	D	GTAW	111.8	42.8	51	45.1	85/87
30	A	SMAW	113.3	69.0	41	37.9	97
	B	SMAW	110.3	52.1	49	45.5	91
	C	SMAW	117.7	52.3	21	20.6	94/95
	D	SMAW	96.2	47.0	13	12.2	91/93

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\*A = As Welded

\*B = Welded + Annealed 2200°F/1 h, WQ

45 \*C = Welded + Annealed 2200°F/1 h, WQ + Exposed 1550°F/1000 h, AC

\*D = Welded + Annealed 2200°F/1 h, WQ + Exposed 1832°F/1000 h, AC

50 The subject alloy can be melted in conventional melting equipment such as air or vacuum induction furnaces or electroslag remelt furnaces. Vacuum processing is preferred. The alloy is useful for application in which its predecessor has been used, including gas turbine components such as combustion liners.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as claimed herein, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention.

## Claims

1. A nickel-chromium-molybdenum base alloy characterized at temperatures of 1800°F and higher by  
 5 (i) a high level of structural stability as determined by its ability to absorb energy over prolonged periods of  
 time of at least 3000 hours at such temperatures, (ii) good ductility together with satisfactory (iii) tensile  
 strength and (iv) stress-rupture strength as well as (v) resistance to oxidation, including cyclic oxidation, said  
 alloy consisting of about 19 to 30% chromium, less than 0.25% silicon, 0.05 to 0.15% carbon, 7.5 to 9%  
 molybdenum, about 7.5 to 20% cobalt, up to 0.6% titanium, about 0.8 to 1.5% aluminum, up to 0.006%  
 boron, up to 0.1% zirconium, up to 5% iron, up to 5% tungsten and the balance being essentially nickel,  
 10 said alloy being further characterized by an average grain size coarser than about ASTM 5.

2. An alloy according to claim 1 in which the percentages of silicon and molybdenum are correlated as follows:

	<u>% Silicon</u>	<u>% Molybdenum</u>
15	0.01 to 0.01	less than 9
	0.1 to 0.15	less than 8.75
	0.15 to 0.25	less than 8.5

20 3. An alloy according to claim 2, consisting of about 20 to 30% chromium, silicon up to 0.15%, about 0.05 to 0.1% carbon, about 7.5 to 8.75% molybdenum, about 7.5 to 20% cobalt, up to about 0.6% titanium, about 0.8 to 1.5% aluminum, up to about 0.006% boron, up to about 0.1% zirconium and the balance essentially nickel.

25 4. An alloy according to any preceding claim in which the silicon content is less than 0.1%, the carbon is from 0.05% to 0.07%, and the molybdenum is at least about 8%.

5. An alloy according to any preceding claim in which the chromium content is from 19 to 23%, and the content of iron, if present, is not greater than 2%.

6. An alloy according to any preceding claim in which the average grain size is from ASTM 1.5 to 4.5.

30 7. A method of producing an alloy according to any preceding claim which includes a final annealing treatment at a temperature above about 2000°F and less than about 2150°F.

8. A method according to claim 7 in which the final annealing treatment is performed at 2025 to 2125°F.

9. A process according to claim 7 or claim 8 in which the alloy composition, grain size and annealing treatment are so correlated that the alloy has a Charpy-V-Notch impact strength of at least 30 ft.lbs. when exposed at 1832°F for a period of 10,000 hours.

35 10. A process according to claim 9 in which the correlation is such that the alloy has a Charpy-V-Notch impact strength of at least 50 ft.lbs. when exposed at 1832°F for a period of 10,000 hours.

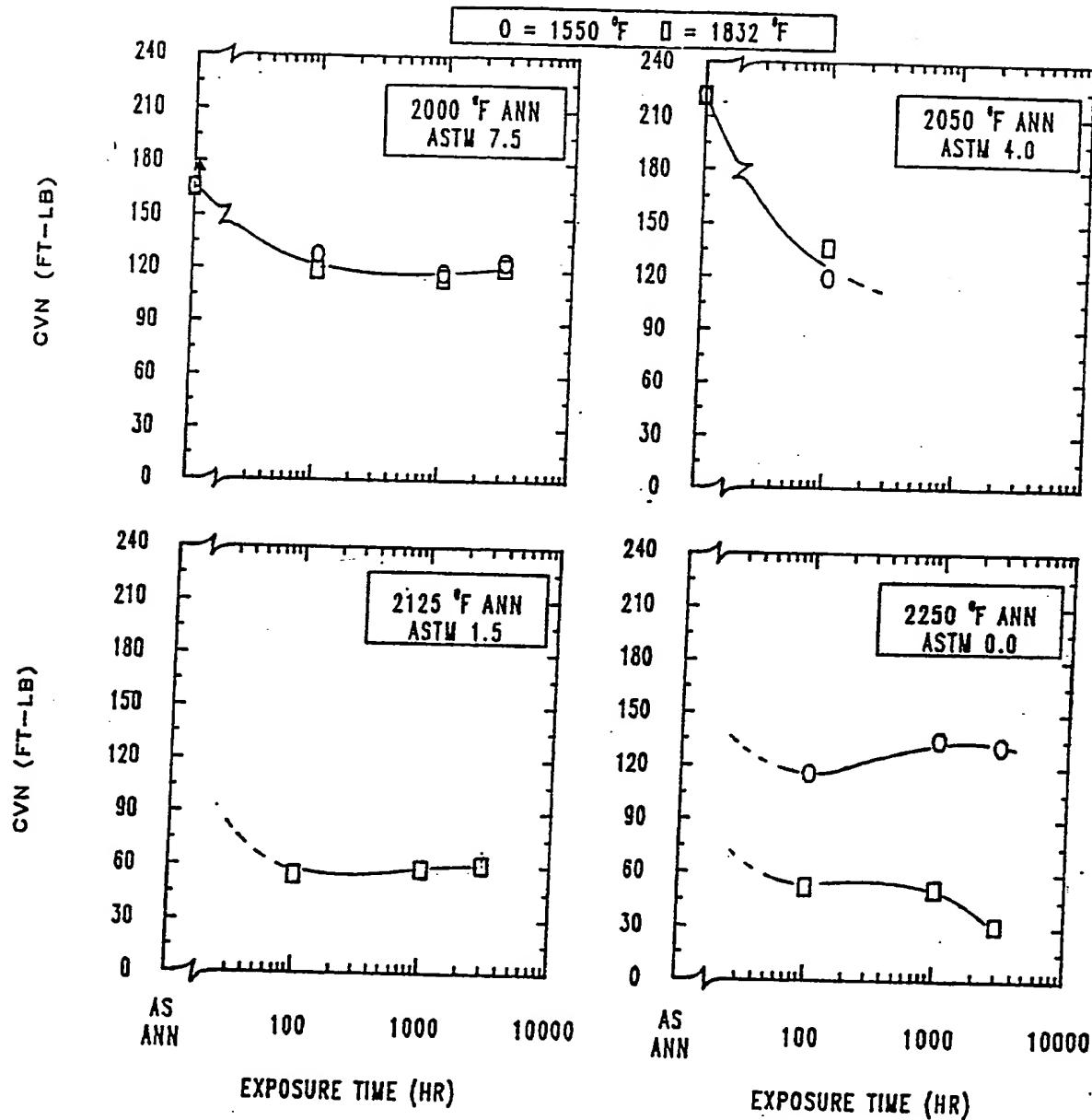
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FIGURE 1  
EFFECT OF EXPOSURE TIME  
ON IMPACT ENERGY





Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑪ Publication number:

0 260 600  
A3

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number: 87113242.9

⑮ Int. Cl. 4: C22C 19/05

⑭ Date of filing: 10.09.87

⑬ Priority: 12.09.86 US 907055

⑦ Applicant: Inco Alloys International, Inc.

⑭ Date of publication of application:  
23.03.88 Bulletin 88/12

Huntington West Virginia 25720(US)

⑬ Designated Contracting States:  
AT BE DE ES FR GB IT SE

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18.01.89 Bulletin 89/03

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⑮ High temperature nickel base alloy with improved stability.

⑯ A nickel-chromium-molybdenum base alloy characterised by exceptional structural stability when exposed at temperatures upwards of 1800 °F (980 °C) for prolonged periods of time, such as 10 000 hours, and consisting of about 19 to 30% chromium, less than 0.25% silicon, 0.05 to 0.15% carbon, 7.5 to 9% molybdenum, about 7.5 to 20% cobalt, up to 0.6% titanium, about 0.8 to 1.5% aluminum, up to 0.006% boron, up to 0.1% zirconium, up to 5% iron, up to 5% tungsten and the balance being essentially nickel, said alloy being further characterized by an average grain size coarser than about ASTM 5.

EP 0 260 600 A3



EP 87 11 3242

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	FR-A-2 149 935 (H. WIGGIN AND CO., LTD) * Claims 1-5 * & US-A-3 859 060 (CAT. A,D) -----	1-6	C 22 C 19/05
TECHNICAL FIELDS SEARCHED (Int. Cl.4)			
C 22 C 19/05			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	19-10-1988	LIPPENS M.H.	
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